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Changes in Conductivity, Alkalinity, Calcium, and pH during a 50-Year Period in Selected Northern Wisconsin Lakes

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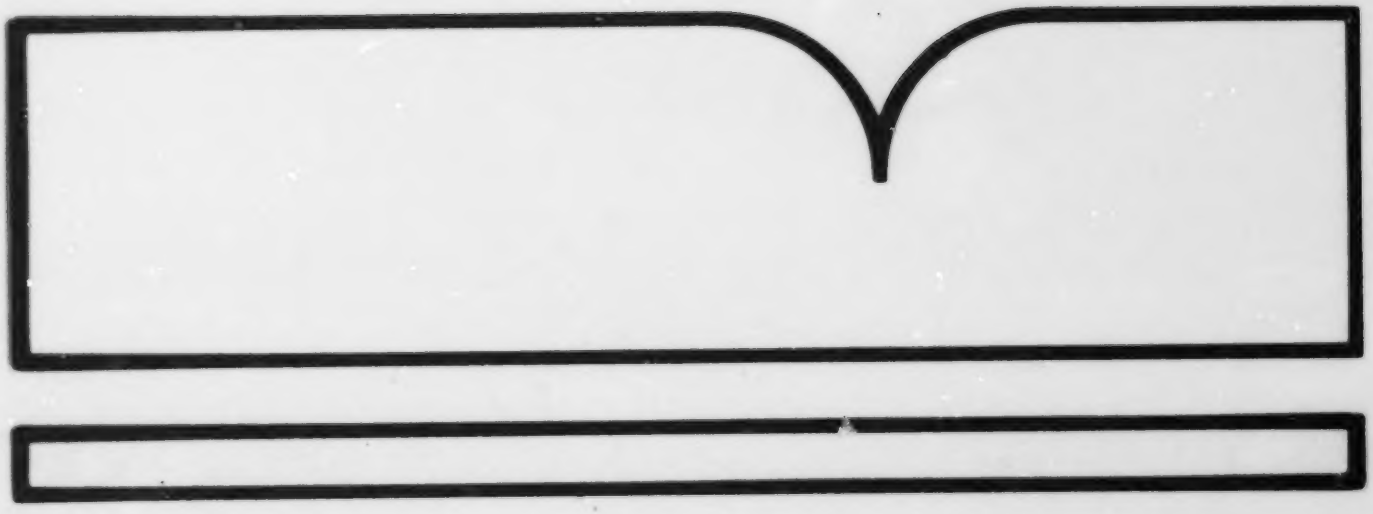

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16. ABSTRACT

Between 1925 and 1941, E. A. Birge, C. Juday, and co-workers in Wisconsin made extensive water quality measurements on over 600 northern Wisconsin lakes, providing a benchmark against which comparisons can be made if the modern equivalent measurements can be determined. Of these, 149 lakes were sampled from 1979 to 1983. Data on conductivity, alkalinity, calcium, and hydrogen ion (pH) are available for these lakes from 1925 to 1931. The historical methyl orange alkalinity data were adjusted to be comparable to the recent Gran alkalinity data by subtracting 57 μmol/L from the historical measurements. The colorimetric historical pH measurements were adjusted to be comparable to recent potentiometric measurements by a regression model. No adjustments were made to the historical calcium or conductivity measurements. Comparisons of adjusted historical data with recent data show a significant increase in the means of all four variables. The largest increases in all four variables show an association with increases in land use development on the lake perimeters. Statistically significant changes in alkalinity are observed, with 28 lakes increasing and 11 decreasing, compared with 110 lakes showing no change. Possible explanations for chemical changes in those lakes that have experienced little change in land use are discussed. For the lakes in northern Wisconsin which may have been affected by airborne pollutants, it is likely that these effects had their beginning before initiation of the historical lake survey.

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Changes in Conductivity, Alkalinity, Calcium, and pH During a 50-Year Period in Selected Northern Wisconsin Lakes

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Between 1925 and 1941, E. A. Birge, C. Juday, and co-workers in Wisconsin made extensive water quality measurements on over 600 northern Wisconsin lakes, providing a benchmark against which comparisons can be made if the modern equivalent measurements can be determined. Of these, 149 lakes were sampled from 1979 to 1983. Data on conductivity, alkalinity, calcium, and hydrogen ion (pH) are available for these lakes from 1925 to 1931. The historical methyl orange alkalinity data were adjusted to be comparable to the recent Gran alkalinity data by subtracting 57 μmol/L from the historical measurements. The colorimetric historical pH measurements were adjusted to be comparable to recent potentiometric measurements by a regression model. No adjustments were made to the historical calcium or conductivity measurements. Comparisons of adjusted historical data with recent data show a significant increase in the means of all four variables. The largest increases in all four variables show an association with increases in land use development on the lake perimeters. Statistically significant changes in alkalinity are observed, with 28 lakes increasing and 11 decreasing, compared with 110 lakes showing no change. Possible explanations for chemical changes in those lakes that have experienced little change in land use are discussed. For the lakes in northern Wisconsin which may have been affected by airborne pollutants, it is likely that these effects had their beginning before initiation of the historical lake survey.

Entre 1925 et 1941, E. A. Birge, C. Juday et leurs collègues ont réalisé un nombre considérable de mesures de la qualité de l'eau dans plus de 600 lacs du nord du Wisconsin; ces mesures, véritables points de référence, permettent d'établir des comparaisons là où les mesures actuelles équivalentes peuvent être déterminées. Ainsi, 149 des lacs déjà échantillonnés, l'ont été de nouveau entre 1979 et 1983. Il existe des données pour ces lacs sur la conductivité, l'alcalinité et la teneur en calcium et en ions hydrogènes (pH) pour la période de 1925-1931. On a soustrait 57 μmol/L des données d'alcalinité de cette époque (méthylorange) pour permettre de les comparer aux données récentes (méthode de Gran). Un modèle de régression a servi à rendre comparable les mesures colorimétriques précédentes du pH aux mesures potentiométriques récentes. Les mesures de conductivité ou de teneur en calcium les plus anciennes n'ont pas fait l'objet de corrections. Les comparaisons de ces données corrigées et des données récentes indiquent une augmentation significative de la moyenne pour les quatre variables. Les plus importantes augmentations, chez les quatre variables, sont liées à un accroissement de l'utilisation des terres en bordure des lacs. Des variations statistiquement significatives de l'alcalinité ont été observées : l'alcalinité augmente dans 28 lacs, diminue dans 11 et reste semblable dans 110. On présente les raisons possibles expliquant les variations chimiques observées dans les lacs autour desquels l'utilisation des terres a très peu changé. Dans le cas des lacs du nord du Wisconsin qui auraient pu être touchés par les polluants atmosphériques, il est probable que ces effets aient commencé à se faire sentir avant le premier échantillonnage.

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The acidification of lakes in industrialized countries of Europe and North America caused by atmospheric deposition has been well documented (Martin 1987). Within the Upper Midwestern portion of the United States, several investigators have identified lakes which also appear, in part, to have been acidified by atmospheric deposition (Schnoor et

al. 1986; Nichols and McRoberts 1986; Eilers et al. 1988). Although the sulfate deposition in the eastern United States has been decreasing in the last decade, large portions of the United States continue to receive deposition acidified by anthropogenic sources (National Research Council 1986; Glass et al. 1986). Northern Wisconsin receives an annual precipitation of 80 cm, with an average pH of 4.7 (1979–82) and an estimated SO_4^{2-} wet deposition rate of 17 kg/ha (Glass and Loucks 1986). These values in Wisconsin approach the pH of precipitation observed to cause lake acidification in Norway (Wright and Henriksen 1978).

From 1925 to 1941, Birge, Juday, and co-workers amassed water quality data on over 600 northern Wisconsin lakes (Frey 1966). The common water chemistry measures (e.g., pH, conductivity, and alkalinity) available for many of these lakes provide a benchmark against which direct comparisons can be made with recent lake water quality data if the modern equivalents of these historical measurements can be determined. Thus, in proposing to examine whether acidification or alkalinization of lakes has taken place in northern Wisconsin between the historical and recent periods, several questions must be explored. The first of these is methodological. What considerations are necessary before presenting historical data in a form comparable to equivalent modern data within a specifiable confidence limit? The second question applies to the gross patterns of water quality changes that may be found over the 50-yr period. What water quality changes have been observed in what lakes, and what methods are appropriate for summarizing the observations? Finally, how has the broad and sometimes opposing mix of anthropogenic alterations (logging, regrowth, cultural eutrophication, and acidic deposition) combined with a variety of mediating processes within the watershed (hydrologic, geochemical, and biotic) to produce the responses observed? Fortunately, the rich 1930's data base for northern Wisconsin and a substantial recent record allow some of these questions to be addressed.

The objective of this paper is to examine the first two of the issues raised above: methodological problems, and overall patterns of change. The paper also develops a general background for evaluation of the mechanisms by which the observed changes could have been induced.

Methods

A comparative analysis of chemical data on lakes over a period of 50 years requires, first, the assurance that the same lakes are being measured, and secondly, that the analytical methods are comparable.

Lake Identification

To satisfy the requirement that any comparisons of lake chemistry must be made with data from the same lake, we first confirmed lake identification. Since the historical lake survey was initiated in the 1920's, approximately one-third of the lakes sampled by Birge and Juday have undergone changes in name. In addition, the study area contains several thousand lakes and, as a consequence, there are numerous cases of duplication of lake names. Because of the changes and redundancy in names, other information was required to confirm the identity of a lake. For example, lake morphometry, proximity to landmarks, and legal descriptions were used to confirm lake identification including the notes, hand-drawn maps, and location descriptions of the original investigators, land use economic inventory maps of the period, 1925 county plat books, county surface water resources inventories, early USGS planimetric maps, aerial photographs, early county soil surveys, and the official record of lake and stream name changes. Conflicts in lake identification among these sources were sometimes resolved by an examination of the water chemistry data where, for example, a softwater lake could easily be distinguished from a hardwater lake of the same name. The process of confirming lake identification led to the exclusion of several lakes from this comparison, because identification could not be made with certainty. The lakes were probably sampled by Birge and Juday, but there was insufficient evidence for confirmation. The documentation for the lake identification task is described more fully in Johnson (1984).

Selection of Study Lakes

The lakes were initially selected for comparison based on the availability of both historical pH and alkalinity data for lakes sampled from 1925–1941 and recent data from summer and fall surveys in 1979 (Eilers et al. 1983a). However, we sought to increase the number of softwater lakes available for comparison by sampling an additional 59 lakes in the summer of 1980 for which historical data were available. The 1980 survey was also designed to address questions of temporal and spatial variability in the lakes and differences in analytical methodology. Those softwater lakes, defined as historical alkalinity < 200 μmol/L, that had multiple historical observations were favored over other lakes. The recent period of record was extended by including data for several lakes through the summer of 1983. Of the 161 lakes with both recent and historical pH and alkalinity data, 10 lakes were excluded from the study based on suspected analytical errors in the historical data. Two lakes were excluded because of possible analytical errors in the recent data leaving 149 lakes available for comparison. A listing of the study lakes and the associated historical and recent data summarized here are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Historical Methods

Juday, Birge, and coworkers, as part of the Wisconsin Geological and Natural History Survey (WGNHS), sampled lakes in northern Wisconsin and compiled a database with about 2000 surface water observations on over 600 lakes (Juday and Birge 1930, 1933; Freeman et al. 1933; Meloche and Setterquist 1933; Juday et al. 1935, 1938). Although the data collection period spans 17 yr (1925–41), 72% of the surface observations were made during the first 6 yr of the survey. Over 90% of the samples were collected during the summer. The water samples were usually collected near the center of the lake with a brass Kemmerer sampler; one portion of the sample was used to fill a soda pop bottle with a tight spring-top cap for dissolved gas analysis while another portion was used to fill a BOD bottle and was covered with a rubber stopper. The samples were kept in the dark, unrefrigerated, and were transported to the Trout Lake Limnological Laboratory for analysis. Where analysis of cations or anions was desired, approximately 100 L was collected, transported to the laboratory in milk cans, and evaporated in porcelain dishes over gas stoves. Laboratory notebooks indicate that many of the samples were analyzed within 24 h for the most common parameters and were usually analyzed 1–3 h after

being returned to the laboratory (R. Pennak, University of Colorado pers. comm.).

Historical conductivity was measured with a portable Digby and Biggs Dionic Water Tester (Evershed 1910) and reported at 20°C. The meter they apparently used was a low-range model measuring from 0 to 200 μS/cm. The limit of error for this instrument "does not exceed 5%; usually it falls between 0 and 3%" (Juday and Birge 1933). A high-range (> 200 μS/cm) Dionic Water Tester was calibrated against standard KCl and NaCl solutions. No bias was observed with this instrument and we have no reason to suspect that the low-range meter did not measure accurately as reported (Emmling and Andren 1984).

Historical alkalinity was measured by adding methyl orange indicator and titrating a 100-mL sample with 1/44 *M* HCl to a "faint pink endpoint" (Juday et al. 1935). This general procedure was apparently followed throughout the lake survey project, except during 1932 when the samples were titrated to a deep, stable pink endpoint. The excess alkalinity from overtitrating during 1932 was corrected by subtracting the amount of acid required to neutralize the additional amount of indicator. Juday et al. (1935) refer to the alkalinity as a "field" measurement, but they apparently meant their field laboratory at Trout Lake as the site of measurement. This deduction is supported by the records of the laboratory technicians (University of Wisconsin Archives, Madison, WI).

The pH for most of the lake samples was measured at the Trout Lake Laboratory, although some measurements were made on the lake shore (Freeman et al. 1933). From 1925 to 1931, the pH was measured using a LaMotte colorimeter (Juday et al. 1935). During and following 1932, the investigators measured pH both colorimetrically and with a Youden portable meter (W. M. Welch, Co., Chicago). The accuracy of the Youden (quinhydrone) meter is discussed by Perley (1937) and is summarized by Welch (1948). Between 1933 and 1941, the investigators continued to measure pH colorimetrically and potentiometrically, but it is not always clear which method they used for a particular sample.

Historical calcium measurements were made using a modification of the McCrudden method as described in Meloche and Setterquist (1933). An analysis of 11 standard solutions containing 6 different concentrations of calcium yielded a standard error slightly less than 3.5 μmol/L with no significant bias reported (Meloche and Setterquist 1933). It is conceivable that the presence of organic matter could have resulted in a positive bias, but an examination of calcium versus conductivity by color (as a surrogate for organic matter) revealed no interaction. They also report results of an analysis of four dolomitic limestone samples from the U.S. Bureau of Standards with an average deviation within 0.15% of the standard, which would correspond to 3.5 μmol/L of the standard. An examination by Meloche and Setterquist of five paired samples of lake water showed a standard deviation of 9 μmol/L.

Birge, Juday, and co-workers also measured other ions (Cl^-, F^-, $NO_2^- + NO_3^-$, Mg^{2+}, Na^+, K^+), but in our opinion, serious deficiencies in the data prevented the use of this information for comparison. Sulfate was also measured in the historical period, but because of uncertainties in the holding times for some samples (records indicate that some of these samples were transported to Madison in milk containers before analysis) and because of possible interferences from the dissolved organics, we have not included these results for individual lakes. Nevertheless, a comparison of barium sulfate precipitation methodology similar to that used by Juday et al. (1938) with ion chromatography methodology showed no major differences (R. Cook, Oak Ridge National Laboratory pers. comm.). Consequently, we will present overall results comparing the unadjusted historical sulfate values with the recent data.

Recent Methods

The recent lake data that were compared with the WGNHS data were also surface samples collected in the summer (defined as June 30 to September 11 in both the historical and recent data). Unlike the historical samples, the recent samples were collected in 1-L Nalgene bottles (filled to prevent contact with air) and were kept on ice in the dark. Replicate samples were collected for analysis by two laboratories (1) Northern Lake Services, Inc. (NLS), Crandon, WI, and (2) the U.S.E.P.A. Environmental Research Laboratory (ERL-D), Duluth, MN.

Conductivity was measured in the ERL-D laboratory at or near 25°C with a YSI Model 32 meter. Temperature corrections were made using the method described by Sorensen and Glass (1987) and are discussed later. Alkalinity was measured by both ERL-D and NLS chemists. NLS staff measured alkalinity for duplicate samples using the standard EPA low-alkalinity method (U.S.E.P.A. 1979) and using two colorimetric indicator methods of bromcresol green-methyl red and methyl orange (APHA 1971). Because of the uncertainty in endpoint used by Birge and Juday, the recent methyl orange alkalinity was titrated to two endpoints at approximately pH 4.6 and 4.0 using 1/88 *M* H_2SO_4. Consistency in endpoints was maintained by titrating distilled water containing the indicator to the appropriate endpoint and using that color calibrated sample as a reference for the sample titrations. ERL-D alkalinity measurements are total inflection endpoint (TIP) values obtained using an automated titration with 0.010 *M* H_2SO_4, closed to the atmosphere, stirred and titrated to pH 3.8 using a Radiometer ABU 80 autoburette and Model M64 pH meter. All points with pH ≤ 4.5 are used in the Gran endpoint calculation of TIP alkalinity.

Field pH was measured with an Analytical Measurements (Model 707-B) meter with a gel-filled combination probe in 1979 and with an Orion 407A with a glass combination electrode in 1980–83. Field pH measurements served as a check on changes between field and laboratory values and were not used in the comparisons with the historical data. The pH meter used by NLS for laboratory pH was a Fisher Acumet (Model #230) with a gel-filled combination electrode (Fisher E5C). ERL-D used a Radiometer pH meter (Model #M64) with glass and reference electrodes. ERL-D pH measurements were chosen to represent the recent lake chemistry because they are internally consistent with their alkalinity and conductivity measurements. The colorimetric pH was measured at the NLS laboratory using a LaMotte pH color comparator with the following indicators and pH ranges: bromcresol green (4.0–5.4), bromcresol purple (5.2–6.6), bromthymol blue (7.0–7.4), and phenol red (6.8–8.4); the pH ranges and formulations (except bromcresol purple) have remained unchanged since the 1920's (R.H. Hutchinson, LaMotte Chemical, 1982, pers. comm.). Supplemental pH measurements were also performed on lake samples collected in 1982–83 using the following indicators: chlorphenol red (5.4–6.8), methyl red (4.4–5.8), and cresol red (7.2–8.6).

Although the colorimetric and TIP alkalinity measurements and colorimetric and potentiometric pH measurements were performed at different laboratories, comparison of conductivity and potentiometric pH values shows little difference. For example, ERL-D and NLS potentiometric pH values exhibited a

median difference of only 0.065 units and a Pearson correlation coefficient of 0.99.

Cation analysis was performed on acid-preserved aliquots at ERL-Corvallis using inductively coupled plasma/emission spectrophotometry with an Applied Research Laboratory ICP, Model QA 137, optimized for manganese with a sample uptake of 3 mL/min, argon consumption at 17 L/min. Subsequent analyses of the calcium measurements on the ICP indicate that these measurements may have a positive bias (relative to measurements on an atomic absorption spectrophotometer) of approximately 3 μmol/L. Anion analyses were performed at ERL-D using a Dionex ion chromatograph.

Adjustments for Methodological Differences

Conductivity — Conductivity was expressed by the WGNHS in μmhos/cm 20°C, whereas the recent data were recorded in μS/cm at 25°C. Temperature conversions for conductivity usually range between 2 and 3% per degree centigrade (i.e., 10–15% adjustment from 20° to 25°C) (Hem 1970; Lind 1979). Wagner (1971) found that a modified Walden conductance-viscosity relationship (Robinson and Stokes 1968) gave superior results over other temperature conversion methods for natural waters. The equation he used was $K \times \eta^A = B$ where K and η are the conductance and viscosity, respectively, at a given temperature and A and B are constants specific for each lake. This approach allowed us to convert accurately the recent conductivity measurements made at 25°C to conductivity at 20°C using a correction derived by computing the constant A based on the ionic composition of each lake (Sorensen and Glass 1987). The average absolute percent difference using this temperature conversion method compared with that of Juday and Birge (1933) is about 0.3% and is within the precision of their original measurements.

Alkalinity — Two common sources of differences between present and historical alkalinity measurements result from the methods of storing and titrating the sample. Kramer and Tessier (1982) discuss the importance of soft glass in contributing to the alkalinity of water samples left in storage before analysis. They report an average increase of about 13 $\mu mol \cdot L^{-1} \cdot d^{-1}$ over a 3-day period in samples stored in unrefrigerated, new glassware. We made no adjustments for possible alkalinity additions from the soft glass sample bottles used in the historical data set because the period between sample collection and analysis was generally less than one day, and the WGNHS sample bottles were probably well used.

There is clearly an adjustment required between the methyl orange alkalinity (MOA) measured in the historical data and the TIP titrations performed for the recent alkalinity, but little agreement has been achieved in determining what an appropriate conversion should be. Burns et al. (1981) subtracted 32 μmol/L (corresponding to an endpoint of pH 4.38) from the MOA values to compensate for colorimetric versus potentiometric alkalinity. Lewis (1982) assumed an endpoint of pH 4.4 (equal to an adjustment of 30 μmol/L) for the endpoint used by Pennak in the MOA titration. Zimmerman and Harvey (1979) concluded that no conversion could be applied to convert MOA to TIP alkalinity because the low alkalinity systems have significant buffering other than bicarbonate, and consequently, the titrations varied in an indeterminate manner. Kramer and Tessier (1982) found that the relationship between MOA and TIP alkalinity for a diluted Lake Ontario sample was consistent and could be adjusted by subtracting approxin. ely 80 μeq/L from the MOA to equal the TIP titration results. Their analysis assumed that the pink endpoint (pH = 4.0) cited in Standard Methods (APHA 1971) was used. All the above investigators apparently assumed that the slope of the MOA-TIP relationship is one.

We investigated the relationship between MOA and TIP measurements by (1) measuring the MOA of standardized concentrations of $Ca(HCO_3)_2$, (2) measuring both MOA and TIP alkalinity for replicate lake samples, and (3) titrating lake samples potentiometrically with and without methyl orange indicator.

A comparison of standard solutions of calcium carbonate prepared using reagent grade material versus alkalinity measured with methyl orange indicator titrated to a pink endpoint (MOA_p) yields the following regression for alkalinity less than 200 μmol/L (all units in μmol/L):

$$(1)\quad MOA_p = 89\ (\pm 4) + 0.965\ (\pm\ 0.034)\ Ca(HCO_3)_2,$$
$$n = 24,\ r^2 = 0.99,\ P < 0.05,\ s = 12$$

The comparison of MOA_p and TIP alkalinity for multiple lake samples collected on 60 lakes in 1980 yields the following regression (all units in μmol/L):

$$(2)\quad MOA_p = 108\ (\pm\ 2) + 1.111\ (\pm\ 0.018)\ TIP,$$
$$n = 323,\ r^2 = 0.90,\ P < 0.05,\ s = 21$$

The intercept of 108 μmol/L is clearly much greater than one would expect based on the titration shown previously for standard solutions, and corresponds to a pH endpoint of 3.93 (assuming an endpoint of pH 5.00 for TIP). The endpoint derived from equation 2 contrasts sharply with analyses run on the same lake samples for an orange endpoint (MOA_o) (all units in μmol/L):

$$(3)\quad MOA_o = 37\ (\pm\ 1) + 1.042\ (\pm\ 0.015)\ TIP,$$
$$n = 328,\ r^2 = 0.94,\ P < 0.05,\ s = 16$$

The slope for MOA_o versus TIP is less than that for MOA_p versus TIP and is closer to the slope observed for the titrations with standard solutions (equation 1), indicating that the difference between the indicator method and TIP decreases slightly at higher alkalinity. However, the MOA_p bias for lake samples shows increasing departure from TIP at higher alkalinity. A possible cause for this increasing bias may be interference from color in these samples. A one-way ANOVA on the differences between MOA_p and TIP for low color (≤ 20 PCU) and high color (> 20 PCU) for the 1980 lake data shows that the high color group exhibits a 17 μmol/L additional bias ($F = 11.67$, $n = 320$). An analysis of residuals from a comparison of alkalinity and conductivity in the historical data shows a nonsignificant additional bias of 14 μmol/L for the high colored group. The standard deviation of the residuals increased among the color groups, doubling from lowest to highest colored lakes. By contrast, no color bias was observed for the MOA_o and TIP for the recent data.

An analysis of operator variability for MOA titrations showed significantly greater values (differences between MOA and TIP) for operator #2, who on both MOA_o ($F = 11.2$, $n = 327$) and MOA_p ($F = 9.2$, $n = 322$) measured 40 and 35 samples, respectively. Operator #3, who measured 150 samples, typically underestimated both MOA_o and MOA_p, relative to the other three operators. The standard deviations between MOA and TIP for the four operators ranged from 9.8 to 24.1 for MOA_o and 16.0 to 27.5 for MOA_p.

The agreement between the calculated difference of 81 μmol/L by Kramer and Tessier (1982), their measured difference of 82 μmol/L, and our measured value of 89 μmol/L for standardized $Ca(HCO_3)_2$ solutions provides support for a difference between MOA and Gran alkalinity of approximately 80 μmol/L assuming (1) the pink endpoint is used, (2) the endpoint occurs at or near pH 4.0, and (3) natural dilute lake waters mimic prepared bicarbonate solutions. However, the MOA titration provides for endpoints other than 4.0 (APHA 1971). Clark (1927) and Kolthoff (1931) show a color change for methyl orange starting at pH 4.4 and extending down to pH 3 1. The 6th edition of Standard Methods for alkalinity (a copy of which was obtained from the Trout Lake Laboratory), which presumably was used by the early investigators, states that the sample should be titrated to a definite color change (APHA 1925). This lack of explicit direction allowed for considerable interpretation of endpoints.

As a check on whether the methyl orange indicator affected the sample alkalinity, we measured 10 pairs of samples with and without the methyl orange indicator, ranging in concentration from 0 to 126 μmol/L. The difference of only 1 μmol/L was not significant, $P \leq 0.05$. Although methyl orange indicator itself has a pH of 4.2, the potential effect of the indicator is diluted by using only 3 to 4 drops per 100 mL of sample. To evaluate these possible MOA endpoints for Wisconsin lake water, we titrated samples containing methyl orange indicator with the pH electrode and recorded the first significant color change. Two technicians, operating independently, each observed an orange endpoint near pH 4.6 and a pink endpoint at pH 4.0. In addition, both operators detected a very faint pink color near pH 4.3, which is close to the endpoints of pH 4.4 also selected by Lewis (1982) and Burns et al. (1981). These differences in endpoints for MOA titrations are expected, considering the color changes observed throughout a wide pH range; the problem is further compounded by the presence of organic material in lake waters.

The historical records show that there was some dissatisfaction with the MOA endpoint used by the WGNHS during the 1930's (University of Wisconsin Archives). In a letter written to Chauncey Juday, Lowell Taylor explains and interprets the experiments he had conducted during the summer of 1932 regarding alkalinity titrations. Taylor worked as a chemist at the Trout Lake Laboratory for several years, and judging from entries in the laboratory notebooks, was very familiar with the analytical methods of the survey and the chemistry of the study lakes. Taylor, suspecting that the MOA method overestimated true alkalinity, experimented with different corrections for MOA using titrations with methyl orange indicator in distilled water. Taylor recommended to Juday that the bias in the MOA be corrected by subtracting 1.5 mg/L bound CO_2 from the existing titrations (equal to an alkalinity bias of 68 μmol/L). Juday apparently decided against incorporating Taylor's recommendation because the tabulated and published data are not corrected for this difference.

We attempted to resolve the question of which MOA endpoint was used by examining the relationship between conductivity, calcium, and alkalinity in the WGNHS data and comparing the relationship with that observed in the modern data set. Implicit in this approach is the assumption that the pCO_2, dissolved organic carbon concentrations, and metals such as aluminum in the lakes have not changed. A comparison of the historical and recent color measurements for all 149 lakes showed that present color values were generally 30% lower than the historical measurements (recent color = 2.7 (± 1.9) + 0.7 (± 0.03) historical color, $r^2 = 0.80\%$, $s = 18$ PCU). However, evaluation of the published historical method (Juday and Birge 1933) and examination of photographs showing the historical measurement procedure suggests that differences in methodology probably account for the observed differences between historical and modern color. The lakes in the study area are primarily calcium bicarbonate systems; consequently, they show strong agreement between conductivity and alkalinity in the recent data set, with a correlation coefficient of 0.99 (excluding 27 of 149 lakes showing evidence of being impacted by road salt). If we assume that an increase in lake water alkalinity would result in a proportional increase in conductivity, then we should observe no increase in alkalinity for those lakes showing no increase in conductivity. Therefore, the difference between historical and recent alkalinity measurements for lakes showing no change in conductivity should be a result of methodological differences, i.e, it should be equal to the difference between MOA endpoint used historically and the TIP method employed today. Note that the converse of this assumption (i.e., an increase in conductivity will result in an increased alkalinity) is not valid because of the addition of other salts such as NaCl. We defined "no change" in conductivity for this test to represent a change of ≤ 2 μS/cm, which is within the accuracy of the method. This is one-half the value for the 95% conductivity confidence interval for a significant difference based on pooled standard deviations of the historical and recent data sets. A regression equation for predicting present TIP alkalinity from present conductivity for those lakes with no change in conductivity yields the following equation:

(4) TIP Alkalinity, μmol/L =
$-122\ (\pm\ 8) + 11.5\ (\pm\ 0.3)$ Recent Conductivity, μS/cm (@ 20°C)

$n = 45,\ r^2 = 0.98,\ P < 0.05,\ s = 32$

A corresponding regression equation for these same lakes using historical conductivity data determined for this lake data set (i.e., those lakes showing a conductivity change ≤ 2 μS/cm), yields the following equation:

(5) Methyl Orange Alkalinity, μmol/L =
$-68\ (\pm 8) + 11.6(\pm 0.2)$ Historical Conductivity, μS/cm (@ 20°C)

$n = 45,\ r^2 = 0.98,\ P < 0.05,\ s = 34$

Because the slopes in equations 4 and 5 are not significantly different, we can combine the recent and historical data to determine the difference between the MOA and TIP alkalinity. The difference between the alkalinity methods is represented by the value of the indicator or dummy variable (see Snedecor and Cochran 1967, p. 416) of 57 μmol/L.

(6) Combined Alkalinity, μmol/L =
$-181\ (\pm 7) + 57\ (\pm 7)\ X_1 + 11.6\ (\pm\ 0.2)$
Combined Conductivity, μS/cm (@ 20°C)
$n = 90,\ r^2 = 0.98,\ P < 0.05,\ s = 33.$

This approach indicates that the historical MOA endpoint for the WGNHS data corresponds to a pH of about 4.17. This value is higher than the value of 4.04 determined by Kramer and Tessier (1982) and closer to values of 4.3 observed in our laboratory tests and the endpoints of 4.25 selected by Asbury et

al. (1989), 4.4 selected by Lewis (1982) , and 4.38 selected by Burns et al. (1981). A similar regression approach for predicting the difference between MOA and TIP using calcium could not be accomplished because of significant differences in slopes between the historical and recent data sets (1.67 and 1.40, respectively).

Our attempts to resolve the MOA bias for the WGNHS data fall into two groups: (a) those which assume an MOA endpoint, and (b) those which assume that certain components of the historical and recent chemical composition (e.g., pCO_2, weak acids, and metals) of a given lake are unchanged. The latter methods, which will be discussed later, include a nonlinear model relating pH to alkalinity, dissolved CO_2, and weak acid contribution.

The differences in endpoints are expected, considering that any endpoints within a range might be acceptable as defined by the method. The WGNHS technicians employed standardization practices by titrating to a color reference solution. Color distinctions are subjective, consequently requiring color standards, and a large degree of variability and error with the method should be expected among different analysts. It is likely that the WGNHS MOA values represent titrations to a range of endpoints, depending upon the care taken by the analyst in reproducing the color reference standards and the variability introduced by the observer for the colored samples. Without additional evidence to resolve this problem, we have elected to use 57 μmol/L derived by our analysis to correct for the historical alkalinity measurements of Wisconsin lakes, a value close to that recommended by L. Taylor (WGNHS chemist) and intermediate between those used by Kramer and Tessier (1982) and Lewis (1982). This will most likely result in unavoidable over- and underestimations of the historical alkalinity for individual lakes, but we believe it best represents this group of Wisconsin lakes.

Calcium — The accuracy reported for the historical calcium determinations was considered acceptable and no adjustment was made to these values. Relationships of historical calcium with conductivity and alkalinity show different intercepts and slopes compared to relationships among these three variables in the recent data perhaps indicating the need to correct historical calcium measurements, however no basis is available for making a correction. As noted, there may be a slight positive bias in the recent calcium values, but the magnitude of this possible bias (3 μmol/L) does not warrant adjusting the recent data. There were historical and recent calcium measurements for 116 of the 149 lakes.

Hydrogen ion (pH) — The majority of the WGNHS pH measurements is colorimetric (all pre-1932 data and an unknown percentage of 1932–41 data), whereas the recent pH data are available for both potentiometric and colorimetric methods on the same samples. The options we have for comparing pH from the two time periods are to compare (1) historical colorimetric to recent colorimetric, (2) historical colorimetric to recent potentiometric, and (3) the limited data on known historical potentiometric pH to recent potentiometric. Several comparisons of historical pH measurement have not been adjusted for differences between colorimetric and potentiometric methods (Hendrey et al. 1980; Burns et al. 1981; Lewis 1982). Schofield (1982) adjusted Hellige colorimetric measurements to potentiometric pH using a regression equation ($r^2 = 0.96$). Kramer and Tessier (1982) illustrate some of the errors associated with colorimetric methods and propose a method of correcting for these errors, assuming one knows which indicator was used.

We examined the relationship between colorimetric (LaMotte) and potentiometric pH for 316 samples from 59 lakes collected in 1980. The overall fit (Fig. 1a) appears reasonably good ($r^2 = 0.87$). For a subset of these recent samples ($n = 175$), we recorded the type of indicator used for the colorimetric pH measurements. The indicators and their respective Pearson correlation coefficients with potentiometric pH are: phenol red (0.83), bromthymol blue (0.58), bromcresol purple (0.75), and bromcresol green (0.91).

A comparison of the WGNHS unpublished colorimetric and potentiometric pH measured by L. Taylor during 1932 again shows good overall agreement between two methods ($r^2 = 0.85$). However, the agreement between colorimetric and potentiometric pH for a given indicator is in some cases poor: phenol red ($r^2 = 0.74$), chlorphenol red ($r^2 = 0.11$), bromthymol blue ($r^2 = 0.38$), and bromcresol purple ($r^2 = 0.09$). Not only do the individual indicator relationships exhibit fairly weak linearity (with the exception of phenol red), but the slopes of the regressions are significantly greater than one and different in most cases from one another (Fig. 1b). It is worth noting, however, that the r^2 for each indicator depends on the relative magnitude of the accuracy and applicable pH range. For example, if two indicators yield equally accurate results but one covers a pH range larger than the other, then the former will yield a greater coefficient of determination. Detailed evaluations of the problems measuring colorimetric pH at low ionic strength are presented by Clark (1927) and Kolthoff (1931).

Kramer and Tessier (1982) demonstrated the effect a color indicator can exert on a softwater sample by adding bromthymol blue indicator and observing the increase in potentiometric pH over 1 unit. Although this is an extreme example (the authors added bromthymol blue, which has a minimum range of pH 6.0 to a sample with a pH of 5.2), it serves to caution against direct use of colorimetric pH without some knowledge of the limitations of the indicators in extremely soft water. We also observed similar effects of colorimetric indicators on potentiometric pH for sample waters with low ionic strength and for waters in which a large difference exists between the sample pH and the pK of the indicator. The shift in potentiometric pH caused by the colorimetric indicators is greatest between pH 5 and 6 (Fig. 1c). Consequently, for those lake waters that we suspect are most likely to be impacted by acidic deposition (e.g., alkalinity < 40 μmol/L), the probability for large errors in colorimetric pH is greater than for the higher alkalinity lakes.

The problem of colorimetric pH measurement error must have been especially great when measuring the pH of previously unsampled lakes, as the investigators did not have the benefit of previous lake data. Although wide-range pH indicators were available, they still suffered from the same problem in very dilute waters where the pK of the indicator can mask the true pH of the sample. An example of this type of error, which we observed in our recent (1980) data, was the pH determination for Sugar Camp Lake. In measurements of samples for which the lake identity was unknown to the technician, this lake consistently showed a potentiometric pH for the surface waters between 5.2 and 5.4 ($n = 10$), yet the colorimetric pH values ranged from 5.0 (bromcresol green) to 6.7 (bromthymol blue). Conversely, it is also possible to err on the low side with colorimetric indicators. This type of error appears to have been responsible for a large number of low pH observations during the summer of 1930. A check of pH outliers in the historical

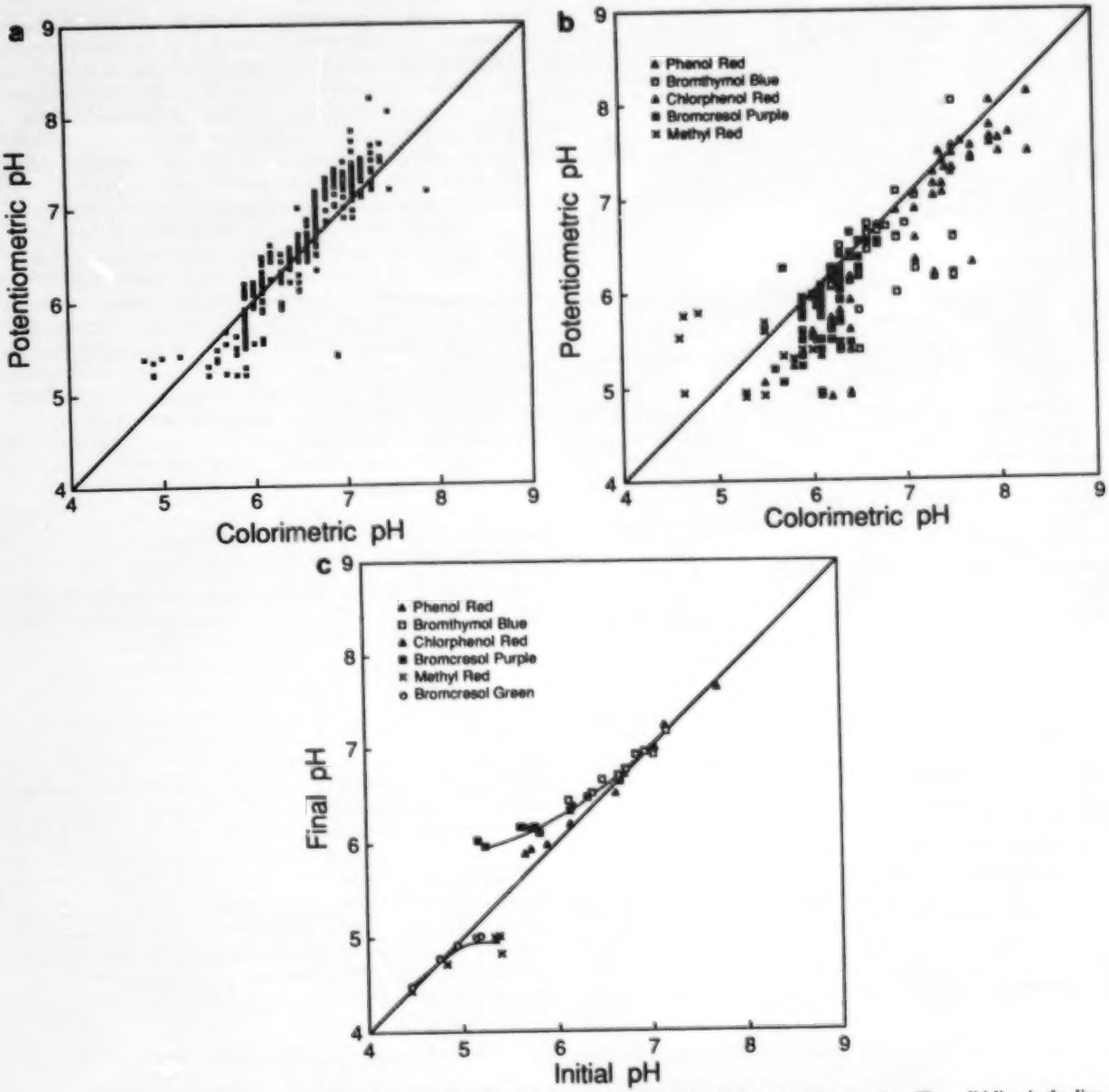

FIG. 1.(a) Recent potentiometric pH versus recent colorimetric (LaMotte) pH for northern Wisconsin lake samples. The solid line is the line of equality. The best fit overall regression model is slope 1.153 (± 0.025) and intercept −0.907 (± 0.166), $n = 314$, $r^2 = 0.87$, $P < 0.01$; (b) Historic potentiometric pH (quinhydrone electrode) versus historic colorimetric pH for five indicators. Regression parameters for individual colorimetric indicators are: bromthymol blue (slope 1.43 (± 0.98), $r^2 = 0.74$, $n = 75$, $P < 0.05$), bromcresol purple (slope 1.67 (± 0.18), $r^2 = 0.61$, $n = 56$, $P < 0.05$), bromcresol green (too few points), and phenol red (slope 0.874 (± 0.167), $r^2 = 0.46$, $P < 0.05$); (c) Effect of color indicators on pH of lake water for six indicators and their respective specified range of operation: bromthymol blue (6.0–7.4), bromcresol purple (5.2–6.6), bromcresol green (4.0–5.4), phenol red (6.8–8.2), chlorphenol red (5.4–6.8), methyl red (10 drops, 4.4–5.8).

study set for lakes with multiple observations showed 24 highly suspicious values (e.g., ≥ 1.0 pH unit from the individual lake mean), only 1 of which was higher than the mean. Of the remaining 23 outliers on the low side, all but 1 occurred in 1930 and only 1 of these was ouside the pH range 5.0 to 5.5. Such a large number of abnormally low values in these lakes strongly suggested operator error in selecting the appropriate pH indicator for the more dilute lakes.

Suspect historical pH and alkalinity data were excluded by fitting the data against a nonlinear model developed for the modern data similar to that used by Small and Sutton (1986). For a given color range, the values of the pCO_2 and weak acid concentration were adjusted to best fit the modern pH-alkalinity data where pH = f(alkalinity, pCO_2, [weak acid]). These fits were achieved using five classes of apparent color, 0 ≤ 2.5, 2.5 ≤ 10.0, 10 ≤ 20, 20 ≤ 60, and > 60 PCU. The resulting

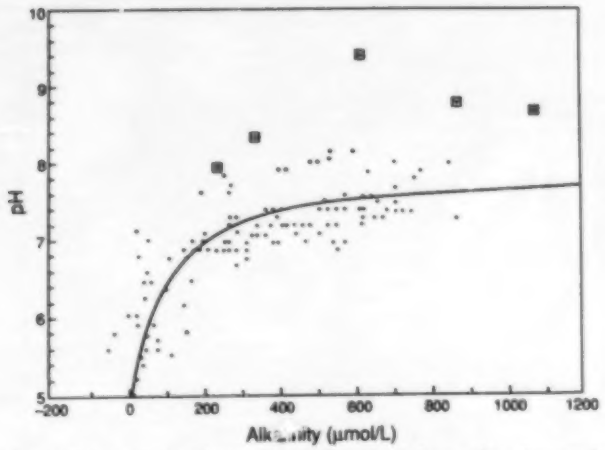

FIG. 2. An example of rejection of historical observations (squares) based on inconsistencies in pH and alkalinity. The curve represents a best-fit nonlinear model that corresponds to a pCO_2 of 3.03 and a weak acid concentration of 81 μmol/L. This example is for lakes with present color from 60 PCU; disassociation constant for weak acids was assumed to be pK 6.0 based on results of fitting modern observations.

pCO_2 values corresponding to these ranges of color were 3.37, 3.33, 3.31, 3.13, and 3.03, respectively. After determining the appropriate model parameters for each color range using modern color data, the historical data (historical color adjusted to correspond with modern color by multiplying historical values by 0.7; see earlier discussion of color measurements), were adjusted for the best fit by allowing a bias to be computed for alkalinity and pH. In this approach, it was assumed that the lakes experienced no systematic change in pCO_2 or weak acid concentrations. Outliers, defined here as those observations 2 SD from the fitted curve, were identified and removed from the set (e.g. Fig. 2).

The computed bias in pH and alkalinity derived from the model-fitting process (Table 1) indicates that the historical pH measurements underestimated true pH, whereas MOA alkalinity overestimated true alkalinity. The clearwater lakes (color ≤ 2.5 PCU) show the least bias in alkalinity, roughly one-half that observed for the colored lakes (color > 20 PCU). Three factors may contribute to this observation: (1) the color of the darkwater lakes may make it more difficult to observe a color change in the methyl orange indicator, (2) the organic compounds in the colored lakes may provide additional buffering to the system, and (3) the bias in the MOA may not be additive, which means that the alkalinity bias cannot be corrected using a constant.

If the alkalinity bias is multiplicative (i.e., the bias is a function of the alkalinity concentration), lakes with higher alkalinity will exhibit a higher bias. Because lakes in northern Wisconsin with higher alkalinity are generally also those with higher color, it is conceivable that the bias is independent of lake color. Regardless of how the historical data are partitioned, historical pH and alkalinity measurements show substantial bias. When averaged across color ranges, the model fitting approach yields a negative pH bias of 0.31 units and a positive alkalinity bias of 57 μmol/L for the raw historical data. These are 0.36 units and 53 μmol/L, respectively, after rejecting outliers identified in the first run. The agreement in alkalinity correction factor of 57 μmol/L between the combined regression analysis approach and this independent nonlinear model fitting approach lends support for the use of 57 μmol/L as the MOA correction factor for this data set.

Methods of Presenting the Most Representative Lake Chemistry for Lakes with Multiple Observations

We examined the variability of surface water chemistry by repeated sampling of 60 lakes in the summer of 1980; one lake was later excluded from the comparison. Fifteen of the lakes were sampled weekly for 10 consecutive weeks while the remaining lakes were sampled three times. At each lake visit, the surface (~ 0.5 m) water was sampled in replicate at each of three locations, forming an equilateral triangle near the center of the lake. The variances of the pH, alkalinity, and conductivity across the three stations were generally much less than the variances across time, indicating that precise location on a lake (within the pelagic zone) probably had little effect on the results. However, some of the lakes showed considerable variation across the summer, particularly in pH. These large fluctuations appeared to be related to photosynthetic activity as indicated by chlorophyll *a* measurements. Individual lake estimates of variability are difficult and costly to obtain; consequently, most general comparisons, including this study, rely on the use of pooled estimates. We did, however, calculate indi-

TABLE 1. Bias in historical pH and alkalinity measurements computed using a nonlinear model for raw and screened data.

		Computed bias					
		pH		alkalinity (μmol/L)		Historical observations	
Modern color range (PCU)	n^a	raw[b]	screened[c]	raw	screened	Rejected	Retained
≤ 2.5	156	−0.44	−0.49	+36	+32	9	147
2.5 ≤ 10	196	−0.35	−0.38	+51	+47	13	183
10 ≤ 20	341	−0.23	−0.27	+59	+57	16	325
20 ≤ 60	254	−0.22	−0.29	+74	+71	15	239
> 60	130	−0.33	−0.38	+63	+58	5	125
Total	1077					58	1019

[a]Using data from the summers of 1925–31 only. Post-1931 pH data were both colorimetric and potentiometric; consequently the computed bias for pH in the later period may differ from pre-1931 measurements.

[b]Using raw historical observations.

[c]After omitting outliers.

vidual lake estimates of variability for those lakes repeatedly sampled in 1980, and compared the results of analyzing the changes in pH with all analyses resulting from pooled estimates. There were only minor differences in the confidence intervals for the three variables for those 59 lakes in which an individual variable was significantly less or greater than the pooled estimate (Eilers et al. unpublished data).

The averages for all parameters represent a simple arithmetic average. It has been common practice to calculate average pH values of lake samples by converting pH values to $[H^+]$, averaging the $[H^+]$, and then reconverting the $[H^+]$ average to pH. At first examination, this approach appears to be correct, since pH units are logarithmic and it is commonly accepted that in making comparisons one should not average log units. Furthermore, it is absolutely necessary to convert pH to $[H^+]$ when computing mass balances such as $[H^+]$ deposition. However, when comparing lake water pH from different dates, it is more appropriate to provide an estimate of the most probable pH. By converting pH values to $[H^+]$ one places more emphasis on the low pH values for a given lake and hence introduces a negative bias in the average pH (Bartlett 1982). Also, because pH is measured in the logarithmic scale, errors in measurement are generally normally distributed in this scale. Average pH is thus a valid statistical method for determining the most probable pH. A more complete discussion of this problem is provided by Boutilier and Shelton (1980).

Land Use Development

Shoreline development defined as the presence of permanent dwellings within approximately 100 m from the lake shore, was used as one factor to evaluate changes in lake chemistry. The number of dwellings present during the historical lake survey was available from state Land Economic Surveys conducted during the 1930's. Recent dwelling counts were made from contemporary USGS topographic maps supplemented by aerial photographs. The median number of shoreline dwellings per lake in the historical period was 4, compared to 26 per lake in the recent period. Thirty-seven lakes in the historical period lacked any shoreline dwelling compared to only 16 lakes in the recent period. For purposes of distinguishing between degrees of increases in shoreline development, we defined three groups of lakes: (1) undeveloped; those lakes with a maximum of one dwelling in either the historical or recent period; (2) moderately developed and (3) highly developed lakes. These were defined on the basis of the recent dwellings normalized by lake area. The highly developed group of lakes defined on this basis had a median of 33.5 dwellings per lake.

Results

The lakes in this study were selected in a non-random manner, which can cause concern about how well the "found" sample reflects the population of lakes implicitly represented by the study. The final set of 149 study lakes, although selected on the basis of data availability and consistency, has chemistry similar to that of population estimates based on the statistical probability sample from EPA's Eastern Lake Survey (Table 2; Linthurst et al. 1986). This latter survey sampled north-central Wisconsin, a subregion that agrees reasonably well with the area of lakes selected for this historical comparison. An estimated 41% of the lakes in the study area had ANC ≤ 50 μeq/L, based on the Eastern Lake Survey, whereas 30% of the lakes in this study group had ANC ≤ 50 μeq/L, (based on the recent data). We believe that the findings from this comparison of historical lake chemistry are generally applicable to other lakes in northern Wisconsin, although the lakes from this study appear to be somewhat more alkaline than a random sample of lakes in this area.

TABLE 2. Mean (and median) present surface water chemistry from this study and from the Eastern Lake Survey.

Variable	This study, Recent Data (n = 149)	Eastern Lake Survey (n = 155, $\hat{N}$ = 1510)[a]
pH[b]	7.03 (7.12)	6.61 (6.67)
Alkalinity (μmol/L)	296 (168)	289 (104)
Calcium (μmol/L)	128 (74)	110 (51)
Conductivity[c]	45.0 (29.0)	40.9 (25.3)

[a]Data from Subregion 2C (Northcentral Wisconsin) where n = sample size; $\hat{N}$ = estimated population of lakes (source: Kanciruk et al. 1986).
[b]Open system pH.
[c]Corrected to 20°C and 25°C, respectively.

Comparison of Historical Versus Recent Measurements

Some indication of variability in the lake chemical data, as well as variability in the changes taking place, can be seen in plots of recent measurements versus historical measurements (Fig. 3). Here, the expected relationship would follow directly along the diagonals in Fig. 3, with the scatter of points on each side being a qualitative measure of lake or sample variability (seasonal or diurnal), differences in analytical methods, or systematic change over time. A bias to one side or the other suggests either a systematic difference in measurements associated with historical versus recent methods or a systematic trend toward elevation or depression in the recent values compared with historical data.

As indicated earlier, conductivity is one variable for which measurement methods have not changed appreciably, but Fig. 3a shows a systematic change toward higher values in the recent measurements. Apparently, most lakes have experienced small to relatively large increases in this variable. Of course, any one of several factors, including application of road salt, cultural eutrophication, changes in hydrology, or ion addition from atmospheric inputs all contribute to the observed effect. Indeed, 27 lakes had the combination of (1) major increases in conductivity, (2) increases in calcium, and (3) a significant length of paved roadway that is maintained in the winter; these lakes are suspected of having been influenced by runoff containing both $CaCl_2$ and NaCl from the deicing chemicals. When these sites are removed, the resulting regression is more tightly aggregated (r^2 = 0.98), has a slope of 1.03, and has an intercept of 3.5 μS/cm 20°C), s = 3.9.

The scatter on both sides of the diagonal for alkalinity and calcium (Fig. 3b and 3c) may represent random error or a pattern in which some lakes have decreased in the recent alkalinity value, while others have increased. Both are possible, because of the opposing effects of forest aggradation versus logging on soil CO_2 concentrations, and other human influences. Calcium, like alkalinity, appears to have increased across a wide range of concentrations. Indeed, the slope of the regression line (1.13) and the intercept (28 μmol/L) suggests that the higher the his-

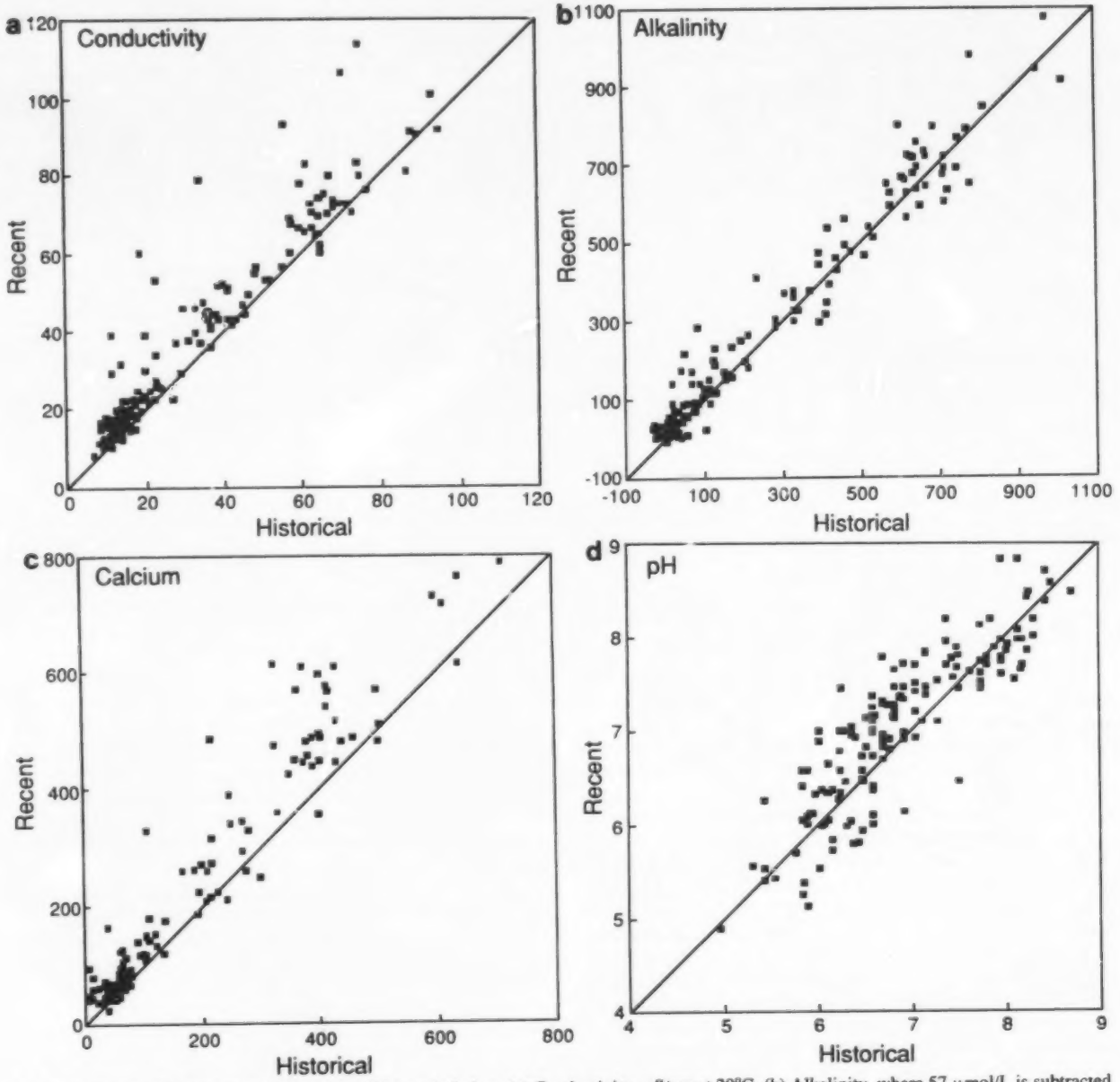

FIG. 3. Water quality changes in 149 northern Wisconsin Lakes. (a) Conductivity, μS/cm at 20°C; (b) Alkalinity, where 57 μmol/L is subtracted from historical values; (c) Calcium, μmol/L; (d) pH, where historical values have been adjusted using this regression equation (pH = 1.19–1.17 [historical]).

torical calcium concentration in the water, the larger has been the increase in calcium.

The broadest scatter of all is in the pH measurements (Fig. 3d). This is not unexpected, given the difficulties in resolving differences between potentiometric and colorimetric measurements, the high temporal variability, and the inherent problems of measuring pH in dilute solutions. The relatively large number of depressed pH values in the low pH range could be, in part, the consequence of methodological differences. The large number of sites showing recent increases in pH across the middle range is consistent with the increases in calcium and in alkalinity, but this also may reflect, in part, a systematic underestimation of pH in the historical measurements. The decline in the pH values for historically high pH lakes could result from unusual biological activity at the time of historic sampling, or, more likely, from methodological differences; however, these uncertainties will not greatly affect an interpretation concerned primarily with changes in softwater lakes. Although there is considerable uncertainty in this comparison of pH, a comparison of recent pH measured with comparable indicators and historical colorimetric pH values also shows that pH increased in 49 of the 59 lakes sampled in 1980.

Average Responses

Overall, small to moderate increases in average conductivity, alkalinity, calcium, and pH occurred between the historical and

TABLE 3. Changes in conductivity, alkalinity, calcium, and pH for Northern Wisconsin Lakes[a]

Case	n[b]	Category	Conductivity (μS/cm @ 20°C)			Alkalinity (μmol/L)			Calcium (μmol/L)			pH		
			Historical	Recent	Change	Historical	Recent	Change	Historical	Recent	Change	Historical	Recent	Change
I	149	All lakes (Median)	22.5	29.0	+3.4	125	168	+14	55	76	+16	6.76	7.12	+0.18
		(Mean ± SE)[c]	33.1 (1.9)	38.7 (2.1)	+5.6** (0.7)	267 (23)	286 (23)	+19** (5)	99 (8)	124 (9)	+25** (3)	6.88 (0.007)	7.03 (0.07)	+0.16** (0.03)
		(Range)	7.0:95.0	8.2:113.5	−6.7:44.5	−30:1017	−7:1075	−138:197	4:357	13:393	−25:145	4.97:8.72	4.90:8.84	−1.06:1.19
II	45	"No" change	16.3	16.3	+0.5	58	63	+7	30	34	+13	6.59	6.88	+0.18
		in conductivity	27.4 (3.2)	27.8 (3.2)	+0.4** (0.1)	193 (37)	198 (37)	+5 (5)	67 (12)	84 (13)	+16** (4)	6.71 (0.11)	6.86 (0.12)	+0.15* (0.06)
			7.0:89.8	8.2:90.1	−1.8:2.0	−15:951	−7:939	−94:111	4:307	13:357	−25:133	5.43:8.32	5.13:8.83	−1.06:1.08
III	19	Undeveloped watersheds	14.3	14.7	+0.5	22	29	+10	23	32	+7	6.13	6.27	+0.05
			14.2 (1.0)	15.3 (1.1)	+1.0 (0.5)	43 (13)	62 (14)	+19* (8)	28 (4)	36 (4)	+8** (2)	6.27 (0.09)	6.35 (0.14)	+0.08 (0.10)
			7.0:22.5	8.2:24.5	−1.8:7.8	−12:213	−7:186	−35:129	6:54	13:75	−7:22	5.86:7.05	5.13:7.45	−0.77:1.18
IV	42	Developed watersheds	31.5	44.3	+6.4	221	281	+18	134	137	+20	6.82	7.18	+0.16
			38.1 (3.8)	47.7 (4.3)	+9.6** (1.8)	316 (44)	348 (46)	+32** (10)	131 (18)	163 (18)	+32** (8)	7.02 (0.12)	7.19 (0.12)	+0.17** (0.06)
			9.0:88.0	13.2:113.5	−6.7:41.0	−30:817	2:980	−94:196	7:321	20:382	−25:145	5.32:8.72	5.54:8.84	−0.53:1.08

[a]Changes are reported as present minus historical value. Alkalinity is adjusted by subtracting 57 μmol/L from the historical values. Historical pH values are colorimetric values transformed to potentiometric values by the equation potentiometric pH = −0.907 + 1.153 (colorimetric pH). Averages and standard errors are calculated from 149 single values (either single data points or averages) per lake.

[b]Number of samples for calcium are I, 116; II, 39; III, 18; and IV, 31.

[c]Probability levels are indicated at $P < 0.01$ (**) and $P > 0.05$ (*).

modern period (Table 3). Averages for two subsets of the lakes, undeveloped and developed watersheds, suggest that much of the increase in conductivity and calcium can be attributed directly to cultural development of lakeshores and watersheds. The increase in calcium for the developed lakes is four times that of the undeveloped lakes. Striking increases in lake conductivity for some lakes appear to have resulted from the use of road salt, which began for this area in 1957 (B. Davies, Vilas Co. Hwy. Dep., 1982, pers. comm.). An evaluation of conductivity for lakes in the region using data from county surface resources publications (Black et al. 1963; Andrews and Threinen 1966) indicates that the lakes in the area had experienced little increase in conductivity by the early 1960's. However, data from this study show that conductivity increased over 100% in one lake and over 200% in another, both of which are bordered by highways but are otherwise undeveloped.

In view of the possible importance of summer residence "development," some additional explanation is required. Most lakes in the area have a substantial number of summer residences and readily qualify as developed; only a few lakes, mostly small and isolated, have no development. At the same time, historical changes in local land cultivation, regrowth of the forest following burning, and recent logging near a few lakes are not reflected in this simple grouping. Of the 19 watersheds classified as undeveloped, only one of the lakes shows a significant ($P < 0.05$) increase in conductivity, whereas 91 of 123 developed lakes show statistically significant increases.

As observed for conductivity, all groups of lakes show average increases in alkalinity. Two partially overlapping groups of lakes, those showing no increase in conductivity and those without development, both show an apparent increase in alkalinity, but substantially smaller in the former than the latter. Indeed, both developed and undeveloped lakes show the same average change, but the undeveloped group includes all 11 lakes that had a significant ($P < 0.05$) decline in alkalinity.

The average increases in pH for all lakes are relatively consistent with the observed increases in alkalinity and conductivity. One anomaly, however, is the pH increase in the lakes showing no increase in conductivity and a relatively small average increase in alkalinity (6 μmol/L). The group of lakes showing the greatest decrease in acidity, based on change in $[H^+]$, is the undeveloped set; this group historically had more acidic lakes than the developed set. At the same time, this underdeveloped group has the largest proportion of lakes (~ 35%) that show a decline in pH. Interpretations of these averages across large and diverse groupings of lakes ultimately must be tempered by analysis of changes on an individual-lake basis.

Some lakes are less acidic and more saline than they were 50 yr ago (Table 4). The two lakes with statistically significant decreases in pH do not show concomitant decreases in alkalinity, and of the 46 lakes with significant and insignificant decreases in alkalinity, only 16 have corresponding decreases in pH. Contingency analysis of the increases and decreases among the four variables shows an association between changes in alkalinity and conductivity, but comparisons between other variables were not significant, suggesting an overall independence in the changes in lake chemistry. Obviously pH and alkalinity values in surface waters are not independent, but are closely related chemically. Lack of a strong association between the changes in pH and alkalinity may reflect high uncertainty associated with the historical measurements for pH.

TABLE 4. Number of lakes with significant and insignificant ($P<0.05$) changes in conductivity, alkalinity, calcium, and pH.

	95% Confidence* interval	Decreases		Increases	
		Significant	Insignificant	Significant	Insignificant
Conductivity (μS/cm @ 20°C)	3.98	3	17	67	62
Alkalinity (μmol/L)	54.8	11	35	28	75
Calcium (μmol/L) (n = 116)	28.5	0	16	39	61
pH (stand. units)	1.07	0	55	2	92

*Confidence intervals were based on an analysis of the 59 lakes with repeated samples in the summer of 1980. The 95% confidence limits were calculated from the sum of the pooled variances of the historical and present sampling periods.

Discussion

When this study was initiated, the questions that we posed were:

(1) can the historical data be used to evaluate changes in water quality?

(2) has the chemistry of the lakes changed? and

(3) can these changes be attributed to natural or anthropogenic factors?

We believe that the historical data are generally internally consistent and well correlated with present lake chemistry, thus affirmatively answering our first question about the quality of the historical data. The unscreened historical and recent data (Eilers et al. 1983b) for 161 lakes were also made available to the National Academy of Sciences. These studies indicate that historical pH and alkalinity measures from Wisconsin are adequate to evaluate changes in water chemistry. Kramer et al. (1986) noted that the magnitude of corrections for the historical pH values ranged from +0.5 to −1.25 pH units and that the likely endpoint for historical alkalinity ranged from pH 4.19 to 4.04. Andren and Bischoff (1985) suggest corrections of similar magnitudes. The smaller range in suggested correction values for the historical alkalinity values compared to those for pH support our interpretation that greater confidence can be placed in the alkalinity data. Unlike the Adirondack lakes for which selection of a methyl orange alkalinity endpoint is critical to the interpretation (e.g., Kramer et al. 1986; Asbury et al. 1989), the evaluation of historical change in Wisconsin lakes is relatively insensitive to reasonable variations in titration endpoints. For example, if we had used a correction of 68 μmol/L suggested by Taylor (corresponding to a pH endpoint of about 4.11) to compensate for the overtitration of historical alkalinity, the number of significant decreases in alkalinity would have changed from 11 to 9 lakes.

The changes in lake chemistry (Tables 3 and 4) demonstrate that there have been increases in conductivity, alkalinity, calcium, and pH. Furthermore, the relative magnitude of the increases in conductivity, alkalinity, and pH are generally consistent among these three variables. The calcium increases for cases I, II, and IV (Table 3), however, appear to be greater than expected, given the increases in conductivity and alkalinity. Examination of case II shows an increase in calcium of 16.5 μmol/L, which conflicts with the lack of change in conductivity. On average, calcium increases over 2.5X that of alkalinity (on an equivalent basis), suggesting cation mobilization, possibly coupled with bicarbonate neutralization. However, the increases in these constituents are clearly not uniform among all lakes. Comparison of lakes in cases II-IV with all lakes (case I), reveals some important differences in the lake changes. The undeveloped lakes show no statistically significant change in conductivity, but do show an increase of 1 μS/cm in conductivity, which is 60% of that expected for an increase of 19 μmol/L in mean alkalinity. Although the highly developed lakes (case IV) show an even greater increase in alkalinity than the undeveloped lakes (case III), the relative increase in alkalinity for the developed lakes is actually less than in undeveloped lakes. The latter group also exhibits an apparent increase in calcium of 7–8 μmol/L, yet the calcium increase in the highly developed lakes of 32 μmol/L represents a four-fold increase. The contrast between the relatively small changes in the undeveloped and highly developed watersheds suggests two important findings: (1) lack of a major change in the undeveloped watersheds indicates that atmospheric deposition has not significantly changed the chemistry of the study lakes in the last 50 yr within the errors of this analysis, and (2) the large chemical increases in the highly developed lakes implicate land use practices as a major influence on changing water quality of the area.

These principal findings must be tempered by two concerns. First, limitations in the historical data, although compensated to some degree, remain problematic. The quality of the historical data varies by parameter and can be ranked such that our confidence in individual observations decreases as follows: conductivity >>alkalinity > calcium >> pH. Unlike the other variables, the uncertainty in alkalinity is caused by both analytical uncertainties (e.g., uncertainty in titration endpoints), and because substantial changes in alkalinity can be masked by either decreases in organic acids or increases in metals such as aluminum. For example, alkalinity may be defined as the excess of cations over strong acid anions where:

$$\text{Alkalinity} = \Sigma \text{ cations} - \Sigma \text{ strong acid anions}$$

$$= (2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] + [Al^{n+}] + [Fe^{n+}] + [Mn^{n+}]).$$

$$([NO_3^{-}] + 2[SO_4^{2-}] + [Cl^{-}] + [F^{-}])$$

The presence of organic anions results in a negative bias in ANC titration results, as compared to the above definition (Sullivan et al. 1989). Under this definition, organic anions could be precipitated as organo-metallic complexes with little change in alkalinity. For example, Schafron and Driscoll (1987) reported a reduction in concentrations of dissolved organic carbon for an Adirondack lake that was associated with the formation of alumino-organic solutes. Chemical changes of this type can leave the water more transparent, yet more toxic to fish.

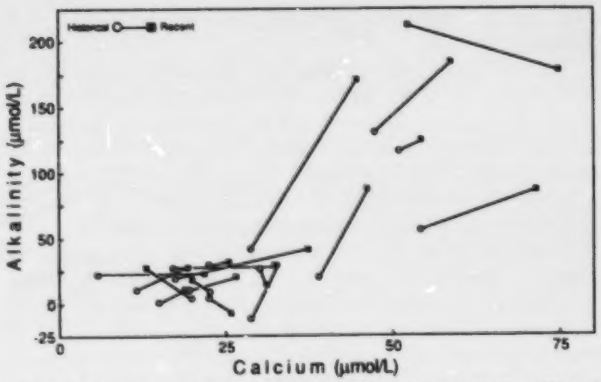

FIG. 4. Changes in calcium and alkalinity (historical alkalinity adjusted by −57 μmol/L) for 18 undeveloped lakes in northern Wisconsin with both historical and recent calcium and alkalinity values. Historical values are shown as open circles; recent values are shown as closed squares.

A second major uncertainty in the analysis is the causality of the changes. The contrast between the responses for the undeveloped and highly developed lakes strongly implicates lake shore development as an important contributing factor to many of the changes. There is considerable evidence from other research that lake shore development promotes increased input of minerals and nutrients to a lake that would have the effect reported here. One problem with the association of lakeshore development and water quality change is that the increase is confounded by hydrologic lake type. Of the 19 undeveloped lakes, 17 are seepage lakes. Because development is more common adjacent to drainage lakes that are typically more alkaline (Eilers et al. 1983a), it is difficult to ascribe the change unequivocally to lake shore development. Also, many other changes occurred in the region during the intervening 50 yr. These additional changes include: (1) major regrowth of the forest cover, (2) dramatic reduction in forest fires, (3) changing SO_x and NO_x emissions, (4) differences in precipitation, and (5) increase in fish stocking and other lake management activities.

Although complete testing of the relationship of each factor to lake change is beyond the scope of this analysis, it is possible to place some of these factors in perspective. Some of the changes are easily associated with a causal factor. For example, the large increases in conductivity exhibited by 27 lakes are clearly linked to the use of de-icing chemicals. For some lakes showing major increases in development, we observe increases in all parameters that could reasonably be attributed to cultural eutrophication. Twenty-one lakes undeveloped in the 1930's experienced increases in the number of shoreline dwellings from 1 to as many as 54; the median increase in the number of shoreline dwellings for all 149 lakes was 20. The 42 highly developed lakes (case IV) experienced increases in alkalinity and calcium twice as great as the remaining 107 study lakes. Although cultural development is implicated as an important factor in chemical changes in many of the study lakes, it is surprising that a comparison of historical and recent Secchi disk values (historical values increased by 5% to account for differences in Secchi disk diameter) reveals no significant differences.

In several watersheds where cultural development has not occurred, substantial increases in chemical constituents were apparently associated with fires that burned a major portion of the watersheds (based on records from the Wisc. Dept. Nat. Resour., Woodruff). Rangeline Lake and Frank Lake are examples of undeveloped watersheds where increases in alkalinity from 12 to 41 μmol/L and from 35 to 171 μmol/L were apparently associated with major fires in their watersheds within the decade preceding the recent surveys.

However, there are few obvious explanations for the chemical changes in the remaining lakes. One could relax the criteria for defining developed lakes and perhaps account for additional lakes that have become culturally enriched. However, the chemical changes for the undeveloped lakes and for the light-to-moderately developed lakes become indistinct.

Another watershed factor that could have a profound influence on lake chemistry is forest regrowth. Most of the virgin white pine forest once covering the study area was completely removed by logging and fires from 1880 to 1920 (Alhgren and Alhgren 1983). The white pine was largely replaced by mixed deciduous forest type, dominated by aspen which was in the early stages of regrowth during the historical lake survey. Replacement of the white pine with deciduous species may have had a major influence on the hydrologic cycle, because the latter species are associated with deeper snowpacks and lower amounts of evapotranspiration. Urie (1967) observed increased groundwater storage under mixed hardwoods compared to pine plantations in a similar hydrologic setting in Michigan. An increase in the groundwater level could have increased the hydraulic gradient, thus increasing the groundwater contribution to the lakes. The importance of groundwater contributions to a softwater seepage lake in the study area was demonstrated by Lin and Schnoor (1986), where the groundwater contributed 3% of the hydrologic input to Vandercook Lake, yet accounted for 24% of the lake alkalinity budget. Lakes that have experienced an increase in both calcium and alkalinity (in the absence of shoreline development) may be reflecting increased groundwater inputs. For several of these undeveloped lakes, concomitant increases in alkalinity and calcium (Fig. 4) are evident. Although one could observe the same response resulting from a change in the chemical composition of the groundwater (Anderson and Bowser 1986), this latter explanation appears unlikely, given the depth of the till in the area and high buffering capacity of the aquifers.

An alternative mechanism for increasing the contribution of groundwater inputs is through increased precipitation. Increased groundwater input to the lakes resulting from an elevated water table could also have resulted from differences in precipitation before and during the respective study periods. Analysis of annual precipitation indicates that from 1917–1937 Wisconsin experienced an extended drought period, with 1923 and 1930 being particularly dry years (Zaporozec 1980). A below-average precipitation period of shorter duration occurred from 1974 to 1976, the latter year having the severest drought on record. However, the precipitation in Wisconsin during the 1970's (including the primary data collection years in the recent lake survey 1979–80), still was above average. Confirmation that the precipitation patterns observed statewide also occurred in the study area was made by evaluating U.S. Dep. of Commerce precipitation records from Rhinelander and other climatological stations in the study area. An analysis of annual precipitation during the historical and recent study periods showed no significant ($P < 0.05$) difference between the periods. When reanalyzed on a seasonal and monthly basis, the recent period had significantly greater precipitation during the summer months. Perhaps of greater importance to the lake and groundwater levels

is the influence of annual precipitation for the several years preceding the lake surveys.

The majority of the lakes show no statistically significant change in the four parameters shown in Table 4. For the small number of lakes that may have decreased in alkalinity and pH, we were interested in determining whether there was an association, if any, with acidic deposition. Recent information on historical emissions of sulfur and nitrogen (Gschwandtner et al. 1985; Johnson 1986) indicates that sulfate deposition may have changed little in Wisconsin between the two study periods and may actually have decreased when considered on a regional basis, assuming that SO_4^{2-} deposition is directly proportional to SO_2 emissions. This assumption is subject to question given the increase in average stack height of the emission sources. A comparison of the historical and recent concentrations of lake sulfate indicates an increase of approximately 5 μmol/L. Nitrogen deposition appeared to have increased several fold and may have acted as an alkalizing factor (see Kilham 1982), presuming that the current ratio of NO_3^-/NH_4^+ was also greater than one. Therefore, if sulfate deposition remained constant or declined and nitrate deposition increased, it would appear that some lakes may have responded by becoming more alkaline. This group of lakes would include those that show an increase in alkalinity without a corresponding increase in calcium. However, this type of chemical response also could be mimicked by fertilization derived from cultural development.

Paleolimnological analyses of nine northern Wisconsin lakes are consistent with a slight acidification of the lakes starting from about 1870 to 1900. Four of the lakes examined showed decreases in pH of about 0.3 units, two lakes showed slight increases, and three lakes showed no significant change (Charles et al. 1989). A recent review of the acid-base status of lakes in the Upper Midwest suggests that acidification has been slight (~ 10 μmol/L) for the most sensitive lakes (Cook and Jager 1989). The magnitude of the loss of alkalinity in the Upper Midwest estimated by Cook and Jager (1989) equals (on an equivalence basis) the estimated increase in SO_4^{2-} for these Wisconsin lakes. If the loss of alkalinity in Wisconsin lakes is associated with replacement by SO_4^{2-}, then lakes showing statistically significant losses of alkalinity during the last 50 yr would be associated with factors in addition to a relatively small acidic deposition signal.

Examination of factors leading to changes in lake chemistry have focused on changes in lake inputs. Another possibility is that some of the lakes have altered as a consequence of within-lake changes in biota. Wisconsin has a long history of active fisheries management (Becker 1983). From the late 1800's to the late 1930's fish were gathered from backwaters on the Mississippi River and other rivers in the state and transported to lakes in northern Wisconsin. This practice supplemented an active fish stocking program begun in the late 1800's. By 1937 Wisconsin established a national record for the propagation and distribution of fish (Wisconsin Conservation Department 1963). Common fisheries practices since the 1940's have included management of the lakes for predator species (e.g., muskellunge, northern pike, walleye, largemouth bass, and trout) with a de-emphasis of the centrarchids native to the lakes. It is conceivable that these widespread biomanipulations have resulted in corresponding shifts in dominant zooplankton and phytoplankton species, which in turn may have altered lake chemistry (Shapiro et al. 1982). An examination of state records (Wisc. Dep. Nat. Resourc., Woodruff, Rhinelander) for 59 lakes sampled in 1980 showed that at least 57 of these had received some form of fish management practice (most commonly, fish stocking).

The chemical record of lakes in northern Wisconsin can be used in a variety of ways to examine changes in lake chemistry over a 50-yr period. The most striking chemical change evident in many of the lakes is an increase in salinity. For those lakes showing statistically significant changes, the evidence strongly supports an alkalinization of lakes associated with cultural enrichment of the lakes from shoreline development. Other factors such as forest fires can account for a smaller number of changes. Most of the remaining lakes show relatively small increases or decreases in alkalinity that, assuming the methodological differences are adequately treated, can likely be attributed to multiple factors, including forest maturation and changes in sulfur and nitrogen emissions. Considering the magnitude and character of the changes that have occurred in northern Wisconsin lakes, it appears that land use changes have the greatest potential for contributing to further changes in the lakes. The large confidence bounds for any single lake computed on the multiple observations in the recent data further suggest that major biological changes would occur in these lakes before statistically reliable changes in lake chemistry could be documented. Given the modest acidic deposition in northern Wisconsin, uncertainty in historical methods, and the multitude of counteracting natural and anthropogenic influences, we cannot attribute the changes in lakewater chemistry to acidic deposition alone.

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